

Photophysical Processes in Polymer Photodegradation, Intrachain Triplet Transfer in Poly(1-Vinylnaphthalene) and Poly(1-Vinylnaphthalene-co-Methyl Methacrylate)

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ABSTRACT

Poly(1-vinylnaphthalene) in a rigid glass at 77° K exhibits a delayed fluorescence due to triplet-triplet annihilation resulting from intramolecular triplet-energy transfer through the naphthalene chromophores. The delayed fluorescence does not appear in the spectrum of 1-ethylnaphthalene. Delayed emission from the polymer but not from the small-molecule analog is quenched by piperylene. End groups are of greater importance than chain length in the control of triplet migration in the homopolymer; experiments with 1-vinylnaphthalene-methyl methacrylate copolymers, however, indicate that a specific minimum chain length is required for efficient transfer.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

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PHOTOPHYSICAL PROCESSES IN POLYMER PHOTODEGRADATION,
INTRACHAIN TRIPLET TRANSFER IN POLY(1-VINYLNAPHTHALENE)
AND POLY(1-VINYLNAPHTHALENE-CO-METHYL METHACRYLATE)

INTRODUCTION

Overt deterioration of polymeric materials through the agency of light either alone or in combination with other causative factors is an extremely complex process. Most investigations are concerned with events taking place long after the process has begun, and, more often than not, secondary reactions are the ones actually observed. An ideal often sought but rarely attained in polymer photolysis is the study of the first-formed free radical; such a study can and has been carried out by irradiating a polymer sample within an electron spin resonance cavity (1). The formation of a free radical by the homolysis of some bond in the polymer molecule is, however, but one possible culmination of a series of phenomena that can follow the absorption of a photon by any substance. These phenomena are termed *photophysical processes*. Their importance to degradation lies in the fact that bond dissociation is only one of several possible consequences of their occurrence. If the energy represented by the initially absorbed photon can be made to follow a path other than the one leading to bond dissociation, the polymer will have been effectively "stabilized" against photodegradation. At the very least, an understanding of these processes as they occur in a polymer should provide a detailed insight into the fundamental reasons for the ultimate event of the bond break which is, in fact, overt degradation.

Briefly, the major photophysical processes are outlined in Fig. 1, in which S_g is the singlet ground state found in most organic molecules, and S_1 , S_2 , T_1 , and T_2 are excited singlet and triplet states, respectively. The latter state is particularly important because of its relatively long lifetime, during which many competing processes have an opportunity to take place. One of these is an intermolecular transfer of energy to a second molecule. The result is that the originally excited molecule returns to the ground state and the second molecule goes to its excited triplet state. Experimentally, phosphorescence from the second molecule will be observed even though the light is initially absorbed by the first molecule. Other photophysical processes can also occur, such as energy transfer from an excited singlet state, which can be demonstrated through fluorescence spectra, or excimer formation, which can be studied through the emission from the complex $[S_1S_g]$ formed by interaction of an excited singlet with a second molecule in the ground state.

The intermolecular transfer of triplet excitation energy in fluid solutions has been an extensively studied phenomenon (2,3). Where the triplet energy of the acceptor is lower than that of the donor molecule, a transfer of triplet energy takes place, probably by an exchange mechanism, on every collision. Triplet exciton migration in crystalline systems is also well established (4). In the latter case, a major requirement is a high degree of symmetry to enhance quantum-mechanical coupling between the triplet states of the individual molecules. If two or more migrating triplet-energy packets are present in the same system, mutual annihilation may take place with the formation of an excited singlet molecule and subsequent delayed fluorescence (5-8).

Interaction between nearby chromophores in a polymer chain to give excimers in fluid solution has been demonstrated by Vala and coworkers (9) for polystyrene and

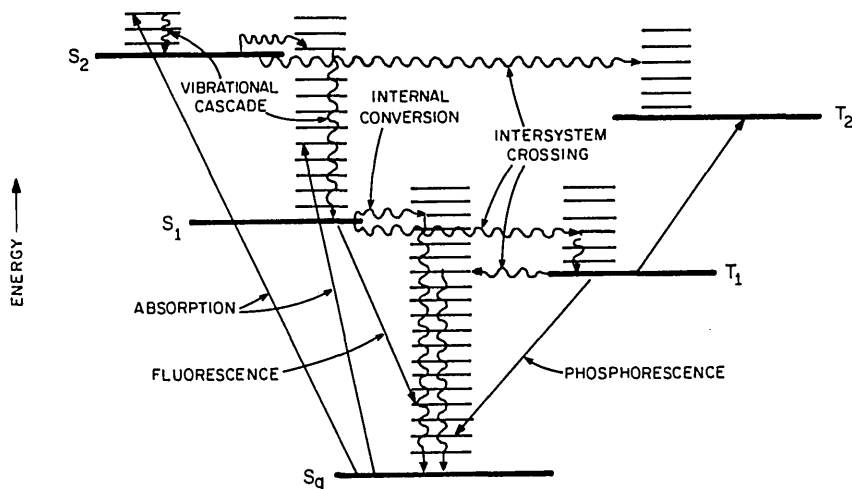


Fig. 1 - Photophysical processes in a typical organic molecule

poly(1-vinylnaphthalene) (PVN). It was suggested (9) that high conformational order would lead to increased delocalization and a corresponding decrease in excimer formation. If a polymer molecule can be viewed as a one-dimensional "crystal," exciton migration should be an important process in the excited chain. Calculations (10,11) regarding exciton band splittings and energy migration in polymer systems indicate that such an assumption may be valid. Singlet exciton band splittings are found to be large, whereas triplet band splittings are small (10). The rate of triplet-triplet annihilation in polymer systems would thus be expected to be less than that observed for pure organic crystals but yet should occur to some extent.

Intramolecular electronic energy transfer has been observed in small molecules consisting of a naphthalene and anthracene group (12) or a naphthalene and benzophenone group separated by one, two, or three carbon atoms (13). In the latter series of compounds it was found that the transfer of triplet excitation energy from the benzophenone group to the naphthalene group within the same molecule was 100% efficient (13). Recent studies (14) of the quenching of phosphorescence of poly(N-vinylphthalimide) by certain introduced impurities indicated the occurrence of triplet-triplet energy transfer along a polymer chain.

EXPERIMENTAL PART

The polymers and copolymers used in this study are indicated in Tables 1 and 2. With the exception of PVN-A and PVN-B, these materials were synthesized from freshly distilled, degassed heart cuts of the appropriate monomers in the absence of air and light. Small amounts of 2-propanol were added as chain stoppers to the polymerization mixtures for PVN-Ib to PVN-Id. The copolymers designated PVN/MMA were prepared from the monomer mixtures in the presence of 0.5% azobisisobutyronitrile (AIBN) by heating at 70°C for 11 hr; conversions were in excess of 50%. Sample PVN-A was a commercial material of unknown history, obtained from Monomer-Polymer Laboratories, Inc. Sample PVN-B was a polymer formed by adventitious polymerization of monomer stored in a refrigerator. All polymers were purified by repeated reprecipitation from tetrahydrofuran or methylene chloride solutions with methanol; the final samples were dried in vacuum at room temperature. No discernible differences were observed among the infrared spectra of the pure PVN samples.

Table 1
Delayed Emission in Poly(1-Vinylnaphthalene)

Polymer	Initiator and Conditions	\bar{P}_n	I_p/I_{df}
PVN-A	*	26.2	2.3
PVN-B	*	17.1	1.9
PVN-Ia	0.5% AIBN, 70°C, 68 hr	21.6	1.0
PVN-Ib	0.5% AIBN, 70°C, 68 hr	22.8	1.8
PVN-Ic	0.5% AIBN, 70°C, 68 hr	20.3	1.5
PVN-Id	0.5% AIBN, 70°C, 68 hr	21.2	2.1
PVN-II	0.5% Bz ₂ O ₂ , 130°C, 5 hr	17.5	6.0
PVN-III	70°C, 68 hr	16.0	12.0

*See text.

Table 2
Delayed Emission in Poly(1-Vinylnaphthalene-
co-Methyl Methacrylates)

Copolymer	$[\eta]$	Average mole-percent VN	I_p/I_{df}
PVN/MMA-Ia	0.084*	99	1.8
PVN/MMA-Ib	0.087	90	1.6
PVN/MMA-Ic	0.13	62	1.6
PVN/MMA-Id	0.23	34	2.3
PVN/MMA-Ie	0.83	7.2	21.0
PVN/MMA-If	0.60†	1.2	75.0

* $\bar{P}_n \approx 21$, calculated as pure PVN (14).

† $\bar{P}_n \approx 2000$, calculated as pure PMMA [H. J. Cantow and G. V. Schulz, Z. Physik. Chem. 1:365 (1954)].

Intrinsic viscosities were determined in benzene solutions at 25°C. Average chain lengths \bar{P}_n for the PVN samples and for PVN/MMA-Ia were calculated from these data with the equation of Loshaek and coworkers (15). Compositions of the PVN/MMA copolymers were evaluated from their ultraviolet absorption spectra in methylene chloride; the compositions corresponded roughly to the initial monomer feed ratios.

Reagent-grade solvents were used; the methylene chloride and methanol were batches selected for their low fluorescence. Diethyl ether and tetrahydrofuran were freshly distilled, the latter from lithium aluminum hydride. The 1:1 mixture of diethyl ether and tetrahydrofuran (9), used in all phosphorescence measurements, formed an excellent glass at 77°K and had a negligible phosphorescence background. The benzophenone was a recrystallized product; piperylene and 1-ethylnaphthalene were commercially obtained and used as received.

Emission spectra were measured at liquid nitrogen temperature on an Aminco-Bowman spectrophotophosphorimeter having a mercury-xenon arc source and a 1P28 detector tube; no corrections were made for either source output or detector response. With the exception of the benzophenone experiment noted below, 290-m μ excitation was used with all solutions. Emission data reported in Tables 1 and 2 were obtained from solutions 10⁻³ M in naphthalene groups. Phosphorescence intensities for a given solution were reproducible within 7%; for a series of solutions of a given polymer, reproducibility was about 10%. The ratios of intensities of phosphorescence to delayed fluorescence I_p/I_{df} are subject to considerably greater error because of the square relationship (see Results) between the two types of emission.

RESULTS

The total emission spectrum of PVN contained peaks for fluorescence (346 m μ) and phosphorescence (490, 525, and 566 m μ) that were nearly the same as those for the small-molecule analog, 1-ethylnaphthalene, although the intensity of the phosphorescence from the polymer was somewhat lower. The delayed emission spectrum of PVN is shown in Fig. 2. Emission having a half-life of approximately 80 msec was observed at 346 m μ , the fluorescence wavelength, in addition to the phosphorescence having a half-life of about 1.3 sec. This delayed fluorescence did not appear in the spectrum of 1-ethylnaphthalene. Triplet involvement in this delayed fluorescence can be inferred from the fact that similar delayed emission spectra resulted from both direct excitation at 290 m μ and excitation of a mixture of PVN and benzophenone at 366 m μ , where PVN does not absorb. Since intersystem crossing in benzophenone is highly efficient, the transfer of energy to PVN must be by way of the triplet states. A plot of the logarithm of the relative incident intensity at 290 m μ against the logarithm of the observed delayed fluorescence was linear and had a slope of 2.0 ± 0.1 , indicating that the process leading to the delayed fluorescence was second order in respect to the intensity of the exciting light.

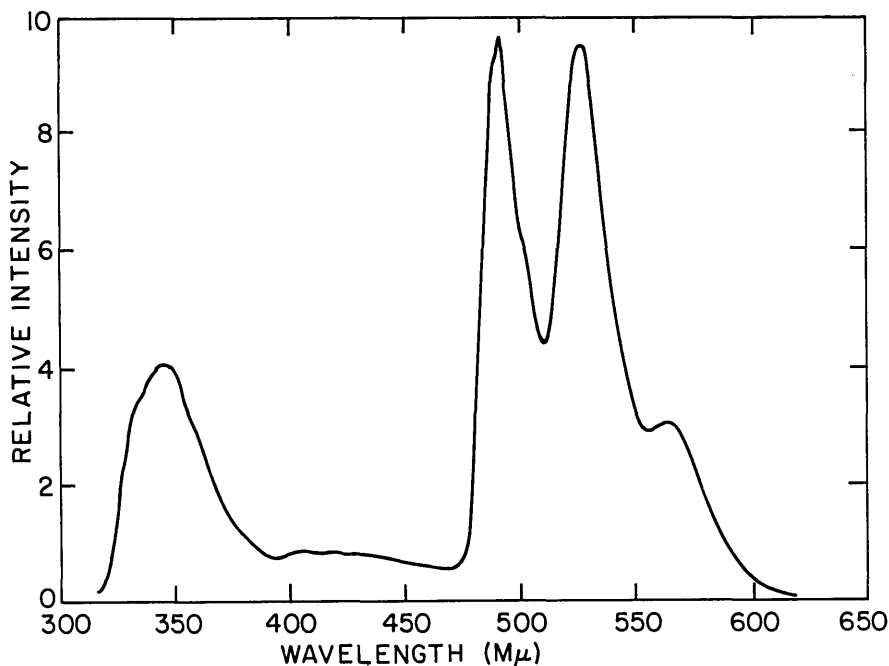


Fig. 2 - Delayed emission spectrum of PVN in tetrahydrofuran-diethyl ether at 77°K; the excitation wavelength was 290 m μ

Piperylene, a well-known triplet quencher, was found to be an effective quencher of both the delayed fluorescence and the phosphorescence of PVN but not of the phosphorescence of 1-ethylnaphthalene at equivalent concentrations. These data are shown in the quenching plot in Fig. 3. No fluorescence quenching by piperylene (16) was observed at the concentrations used in our experiment.

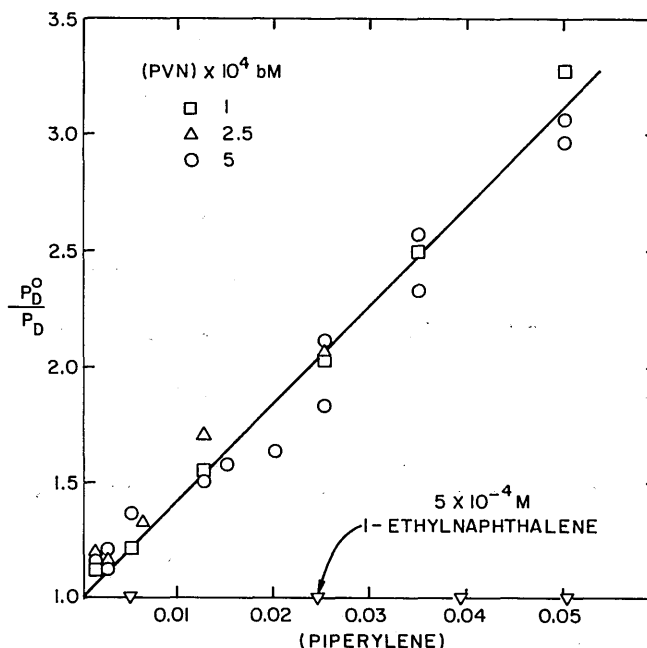


Fig. 3 - Quenching of PVN and 1-ethylnaphthalene phosphorescence at 77°K as a function of piperylene molarity

In Table 2 are shown the values of I_p/I_{df} for a series of 1-vinylnaphthalene-methyl methacrylate copolymers. Copolymer concentrations were made such that each sample was 10^{-3} M in naphthalene groups; approximately the same absolute phosphorescence and fluorescence intensities were exhibited by all of the solutions. Thus, the resulting rigid matrices contained different numbers of polymer solute chains, and the average copolymer chain lengths were different as well. It is evident from Table 2 that, as the average proportion of naphthalene-containing segments drops below about 50 to 60%, the number of triplet naphthalene groups undergoing triplet-triplet annihilation decreases markedly, indicating a statistical minimum in the length of a chain of naphthalene rings which can generate detectable delayed fluorescence.

DISCUSSION

The observations presented above can best be explained by the absorption of two photons by the same polymer molecule, forming excited singlet states which intersystem-cross to the triplet manifold. The triplet excitation energy migrates along the polymer chain by way of the naphthalene rings until the two triplets come in close enough proximity to undergo triplet-triplet annihilation with the formation of an excited singlet and a

ground singlet system. The fluorescence from this excited singlet will appear to be longer lived than that from one directly formed by the absorption of a photon. Many of the triplets phosphoresce before they have an opportunity to undergo triplet-triplet annihilation. The absorption of the second photon by the polymer chain must occur during the average lifetime of a triplet group (ca. 1.3 sec). This series of reactions can be represented by

- | | |
|--|------------------------------|
| 1. ${}^1M_i + h\nu \rightarrow {}^1M_i^*$ | Absorption |
| 2. ${}^1M_i^* \rightarrow {}^1M_i + h\nu'$ | Fluorescence |
| 3. ${}^1M_i^* \rightarrow {}^3M_i^*$ | Intersystem crossing |
| 4. ${}^3M_i^* \rightarrow {}^1M_i + h\nu''$ | Phosphorescence |
| 5. ${}^3M_i^* + {}^1M_{i+1} \rightarrow {}^1M_i + {}^3M_{i+1}^*$ | Triplet migration |
| 6. ${}^3M_{i+n}^* + {}^3M_{i+n+1}^* \rightarrow {}^1M_{i+n}^* + {}^1M_{i+n+1}$ | Triplet-triplet annihilation |
| 7. ${}^1M_{i+n}^* \rightarrow {}^1M_{i+n} + h\nu'$ | Delayed fluorescence |

where M_i represents a chromophore on the i th segment of the polymer, the superscripts 1 and 3 represent singlet and triplet states, respectively, and the asterisk denotes an excited state.

Triplet-triplet annihilation, process 6, is expected to be second order in triplet concentration, and this is borne out by the square relationship between delayed fluorescence and the incident light intensity. If triplet energy were completely localized at the segment which initially absorbed the photon, i.e., if process 5 were not functioning, the observed delayed fluorescence could only result from the absorption of a second photon by a neighboring segment within the lifetime of the first triplet. Not only is this a statistically improbable event, but it is demonstrably unlikely. Emission arising from noninteracting pairs of chromophores in a chain should be as readily quenched as that from the equivalent isolated chromophores under the same conditions. In fact, the perylene quenching experiment (Fig. 3) shows that the delayed emission from PVN is indeed quenched while the phosphorescence from the same concentration of naphthalene rings in the form of 1-ethylnaphthalene is not.

It is evident from the data in Table 1 that something other than chain length controls I_p/I_{df} in PVN homopolymers. A reduction in chain length from 20 units to 16 represents a decrease of 20% in the probability of two photons being absorbed by a single chain; the variation in I_p/I_{df} is on the order of 800%. Since the quenching experiment has eliminated excitation of adjacent rings, which would be independent of chain length, differences in polymer structure may be the source of this variation. For example, PVN-Id, PVN-II, and PVN-III differ in their mode of initiation and thus would be expected to have different end groups. If these end groups possess triplet-energy levels lower than those of the naphthalene-containing units along the chain, migrating energy would localize in the end groups and the efficiency of process 7 would be thereby reduced. Similarly, any defect along the chain that can act as an energy sink will increase I_p/I_{df} . Thus, the wide variation in observed I_p/I_{df} for chemically different kinds of PVN chains supports the notion of highly efficient delocalization of absorbed energy along the chain.

That some minimum chain length containing only naphthalene chromophores is required for detectable delayed fluorescence is shown by the results with the copolymers. Segments of the polymer originating from methyl methacrylate would be expected to act

as barriers to the transfer of energy from naphthalene groups. Statistically, the smaller the proportion of the copolymer having its origin in 1-vinylnaphthalene, the shorter would be the chains containing naphthalene substituents and the greater would be the length of the insulating ester-containing segments. The sudden falloff in delayed fluorescence in copolymers below a specific concentration of naphthalene groups again supports the concept of intramolecular energy transfer in PVN. A more intimate knowledge of the structure of these copolymers is required before detailed comment can be made concerning the role of chain defects in this type of transfer.

Concomitant energy transfer processes involving migration by way of singlet states, for example, have not been eliminated by our investigation. Excimer emission from PVN in fluid solution is readily observed at room temperature but is not seen at 77° K in a rigid glass (9). This has been attributed (9) to a decrease in mobility of chromophores at the lower temperature which tends to prevent the alignment of rings required for excimer formation. Some kind of coupling is required for both excimer formation and triplet migration. This requirement is probably less exacting in the latter case because of the far greater lifetime of the triplet relative to the singlet. In a rigid glass, suppression of excimer formation allows a larger number of singlets to undergo intersystem crossing. The resulting triplets can then transfer their energy to a near-neighbor chromophore. Again, the answers to these questions lie in the specific conformation of PVN chains and chromophores in a tetrahydrofuran-diethyl ether glass at 77° K, detailed knowledge of which we do not now have.

Clearly, the finding that intramolecular energy transfer takes place in PVN has important implications in the field of polymer photodegradation, as well in other areas such as photosynthesis. Wherever such transfers can occur, it is highly probable that the ultimate chain break that represents degradation will occur at a weak link in the chain rather than at a bond in a "normal" segment of the polymer. The weak link could be some impurity, or it could be simply a disorientation in the chain. It could be an end group since end groups affect the transfer; the breaking of a bond at this point may yield a radical which in its turn could attach a second chain. At the same time, polymers in which intramolecular energy transfer takes place may be stabilized to photodegradation by incorporating an energy sink into the chain. Such a sink, if it were an emitter, would not only provide a means of energy release but may provide through an emission study a way to observe variations in the main chain conformations and, in fact, a method for detection of intramolecular energy transfer in polymers where the delayed emission method cannot be applied. This will be the subject of future reports.

CONCLUSION

Intramolecular electronic energy transfer has been found to take place in poly(1-vinylnaphthalene) in a glass at 77° K. This type of energy transfer can be observed through measurements of delayed fluorescence in polymers having suitable spectral characteristics.

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